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## STUDIES ON THE ELECTROCHEMICAL PROPERTIES OF COPOLYMERS OF MALEIC ACID, IV Comparison of Chelate Formation Constant

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The apparent chelate formation constants of alkaline earth metal ions, Ba and Ca, with maleic acid-vinyl acetate and maleic acid-styrene copolymers were evaluated according to Morawetz's method and the comparison between two copolymers was done. At low charge density per carboxyl pair, the formation constant for the styrene copolymer was smaller than that for the vinyl acetate copolymer. At high charge density per carboxyl pair, the reverse relation was obtained. The results were explained by taking the influence of the neighboring ionized groups beyond the comonomer and that of the field effect of polyion into consideration.

### Introduction

The titration behavior of polyelectrolyte in the presence of divalent cations is complicated by the complex formation superimposed on the electrostatic effect. Gregor and co-workers<sup>1)</sup> carried out the titration of polyacrylic acid in the presence of cupric salts and evaluated the formation constants of the complexes formed using a modification of the methods of Bjerrum<sup>2)</sup>.

On the other hand, the chelation of the alkaline earth metal ions by the copolymers of maleic acid was treated quantitatively by Morawetz, Kotliar and Mark<sup>3)</sup>.

In similar 1 : 1 copolymers of maleic acid, it was assumed in the previous paper<sup>4)</sup> that the interaction between the ionized groups on both sides of comonomer differed with the kind of comonomer substituent. The difference in the neighbor interaction may result in the difference of chelate formation constants with alkaline earth metal ion. The present paper will show that the difference between the chelate formation constant of maleic acid-vinyl acetate (MA-VAc) copolymer with barium or calcium and that of maleic acid-styrene (MA-S) copolymer may be explained from the above mentioned standpoint. For this purpose, the chelate formation constants of two copolymers will be evaluated according to the method by Morawetz and co-workers.

### Experimentals

The copolymers used here were the samples of MA-VAc and MA-S copolymers described in

- 1) H. P. Gregor, L. B. Luttinger and E. M. Loebl, *J. Phys. Chem.*, **59**, 34, 366, 559 (1955)
- 2) J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, P. Hase, Copenhagen (1941)
- 3) H. Morawetz, A. M. Kotliar and H. Mark, *J. Phys. Chem.*, **58**, 619 (1954)
- 4) K. Monobe, *This Journal*, **30**, 145, 155 (1960)

Part I<sup>5)</sup> of this series. The experiments to estimate the chelate formation constants were performed by the potentiometric titration of the copolymers in 1 *M* sodium nitrate solution at 20.0  $\pm 0.1^\circ\text{C}$ . The solutions were titrated with sodium hydroxide in the absence and the presence of alkaline earth salt,  $\text{Ba}(\text{NO}_3)_2$  or  $\text{Ca}(\text{NO}_3)_2$ . The concentration of the alkaline earth salts added was  $3 \times 10^{-3} M$  and it was much smaller than the total salt concentration. The apparatus and the detail of titration methods were given in the previous paper<sup>5)</sup>.

### Chelate Formation Constant

The chelate formation constant of alkaline earth metal ions by the copolymer of maleic acid was represented by the following equation by Morawetz and co-workers<sup>3)</sup>;

$$K_f = \frac{[\text{MA}]}{[\text{M}^{++}][\text{A}^-]}, \quad (1)$$

where  $[\text{MA}]$  represents the concentration of carboxyl pairs chelated with alkaline earth metal ions, and  $[\text{M}^{++}]$  and  $[\text{A}^-]$  represent the concentration of free metal ions and free carboxylate anion pairs, respectively. The chelate formation constant represented by Equation (1), however, relates to the stability constant of the whole equilibria shown by the reactions of the type,



where  $k_1$  and  $k_2$  represent the formation constant for each reaction and are  $\frac{[\overset{+}{\text{M}} \overset{-}{\text{A}}]}{[\text{M}^{++}][\text{A}^-]}$  and  $\frac{[\text{MA}]}{[\overset{+}{\text{M}} \overset{-}{\text{A}}]}$  respectively.

Therefore, the stability constant of the chelate ring can be represented<sup>3)</sup> by the equation

$$K_f = k_1 k_2 = \frac{[\text{MA}]}{[\text{M}^{++}][\text{A}^-]}. \quad (3)$$

In monomeric dibasic acid such as succinic acid, the constants,  $k_1$ ,  $k_2$  and  $K_f$  defined above may be expected to be constant. However, in polydicarboxylic acid such as copolymers of maleic acid which contains a very large number of acid groups, this can no longer be expected<sup>1)</sup>.

In particular, the equilibrium constant  $k_2$  is determined by the state of a  $\overset{+}{\text{M}} \overset{-}{\text{A}}$  in itself in the monomeric acid case, but it is affected by the neighboring ionized groups beyond the comonomer on a polymer chain in the latter case. Of course, the neighboring ionized groups beyond the comonomer affect also the constant  $k_1$  in the latter case. However, the contribution of entropy to the constant  $k_2$  may be considered to be smaller than the contribution to the constant  $k_1$ , so that the effect of neighboring ionized groups beyond the comonomer may be larger on  $k_2$  than on  $k_1$ .

On the contrary, the effect of other ionized groups on a polymer chain may be considered to be larger on  $k_1$  rather than on  $k_2$ .

Thus, the intermediate state represented by  $\overset{+}{\text{M}} \overset{-}{\text{A}}$  plays an important role for the present

5) K. Monobe, *This Journal*, 30, 138 (1960)

purpose.

However, the constants,  $k_1$  and  $k_2$ , can not be evaluated separately, as long as Morawetz's method is applied, since the intermediate state in Reaction (2) does not come directly into appearance on Equation (3). In order to evaluate the formation constant  $K_f$ , the author used Morawetz's method here. And the results for two copolymers will be examined from Reaction (2) and Equation (3).

Now, since the chelation is observed only in the second half of the titration curve, it may be assumed that the concentration of un-ionized carboxyl pairs is negligible.

The concentrations of the singly and doubly ionized species,  $[HA^-]$  and  $[A^-]$  are related with the degree of ionization,  $\alpha'$ , by the equations:

$$[HA^-] = C(2 - \alpha') \quad (4)$$

and

$$[A^-] + [MA] = C(\alpha' - 1), \quad (5)$$

where  $C$  is the stoichiometric concentration of carboxyl pairs and corresponds to the polymer concentration.

The average charge  $Z$  per carboxyl pair is represented by the equation,

$$Z = \alpha' - \frac{2[MA]}{C} \quad (6)$$

We shall assume that the free energy of dissociation depends only on  $Z$  at the constant polymer and salt concentrations. According to Morawetz<sup>3,6)</sup>, the following equation to evaluate  $Z$  was presented:

$$\frac{[H^+]}{2 - \alpha'} = \frac{2f(Z) + [H^+]}{Z}, \quad (7)$$

where  $f(Z)$  is the function defined by following equation and is known from the titration data obtained in the absence of chelating ions;

$$\frac{[H^+][A^-]}{[HA^-]} = K_a = K_o \exp(-\Delta F_e/kT) = f(Z), \quad (8)$$

where  $K_a$  is the apparent dissociation constant and is antilogarithm of the value denoted by  $pG_2$  in the previous paper<sup>4)</sup>.  $K_o$  is the intrinsic dissociation constant and  $\Delta F_e$ <sup>7)</sup> is the free energy change due to the displacement of a proton to infinity against the field of all charges on the molecule.

As  $Z$  can be evaluated from Equation (7),  $[MA]$  and  $[A^-]$  are obtained from Equations (6) and (5). The free metal ion concentration  $[M^{++}]$  is the difference between the stoichiometric metal concentration and  $[MA]$ . Thus, the formation constant  $K_f$  defined by Equation (1) or (3) can be calculated.

6) Reference 3); Equation (7) is obtained by proper substitution from Eqs. (4), (5) and (6) into Eq. (8).

7) N. Bjerrum, *Z. phys. Chem.*, **106**, 219 (1923)

## Results and Discussion

The titration data of MA-VAc and MA-S copolymers in the absence and presence of alkaline earth salts are given in Tables 1 and 2. The plots of  $-\log K_a$  as a function of  $Z$  are obtained from the titration data in the absence of alkaline earth salts for two copolymers and illustrated in Fig. 1. The same behavior as that shown in Fig. 1 was given in the previous paper<sup>1</sup>. The occurrence of chelation does not in itself alter the dissociation behaviors of the acid, but results in the change of  $Z$ . The formation constants calculated on the base of these data are illustrated in Figs. 2 and 3.

Table 1 Titration data for MA-VAc copolymer (20°C)

NaNO <sub>3</sub> =1 M Degree of neutralization $\alpha$	$C=1.033 \times 10^{-2} M$	Me(NO <sub>3</sub> ) <sub>2</sub> = $0.29 \times 10^{-2} M$	
		pH	
	reference	Ca <sup>++</sup>	Ba <sup>++</sup>
1.079	4.84	4.75	4.80
1.169	5.20	5.12	5.15
1.258	5.48	5.39	5.45
1.348	5.74	5.64	5.68
1.438	5.99	5.86	5.91
1.528	6.25	6.09	6.15
1.618	6.51	6.31	6.40

Figs. 2 and 3 give the plots of  $\log K_f$  as a function of  $Z$  in the presence of alkaline earth salts, Ba(NO<sub>3</sub>)<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>, respectively.

Table 2 Titration data for MA-S copolymer (20°C)

NaNO <sub>3</sub> =1 M Degree of neutralization $\alpha$	$C=0.948 \times 10^{-2} M$	Me(NO <sub>3</sub> ) <sub>2</sub> = $0.291 \times 10^{-2} M$	
		pH	
	reference	Ca <sup>++</sup>	Ba <sup>++</sup>
1.077	6.11	6.11	6.11
1.175	6.72	6.70	6.71
1.273	7.22	7.17	7.19
1.371	7.66	7.53	7.62
1.468	8.10	7.85	8.01
1.566	8.53	8.17	8.39
1.664	8.95	8.50	8.73

The formation constant  $\log K_f$  increases with  $Z$  for both copolymers. But the result is quite different from that of the monomeric dibasic acids such as succinic acid.

However, if we compare the results for MA-VAc copolymer with those for MA-S copolymer, we can readily notice a fact as follows.

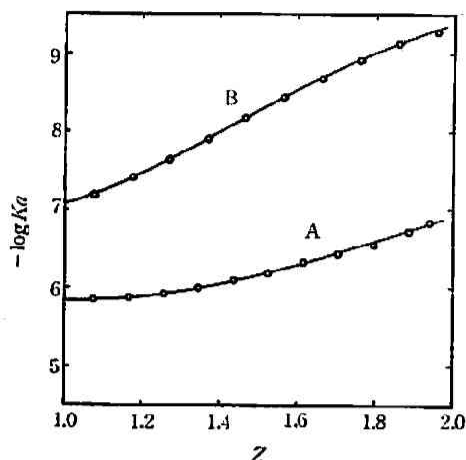


Fig. 1 Plots of apparent dissociation constants against charge density (20°C)

curve A; MA-VAc copolymer 1M NaNO<sub>3</sub> solution

curve B; MA-S copolymer 1M NaNO<sub>3</sub> solution

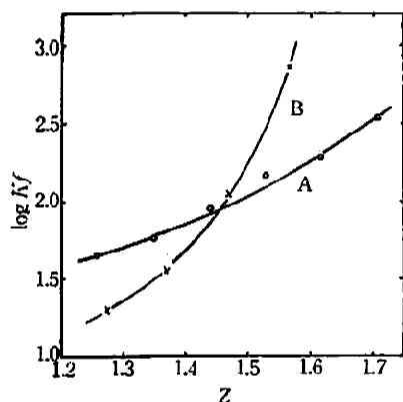


Fig. 2 Chelate formation constants with Ba as a function of charge density (20°C)

curve A (O); MA-VAc copolymer

curve B (×); MA-S copolymer  
Ba(NO<sub>3</sub>)<sub>2</sub> = 0.291 × 10<sup>-2</sup> M

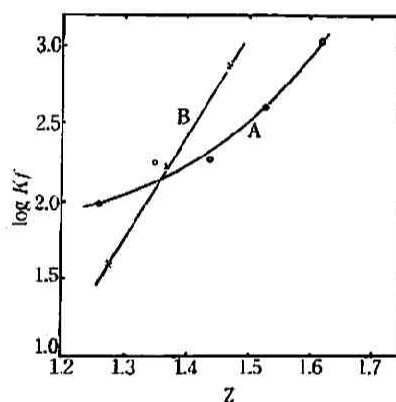


Fig. 3 Chelate formation constants with Ca as a function of charge density (20°C)

curve A (O); MA-VAc copolymer

curve B (×); MA-S copolymer  
Ca(NO<sub>3</sub>)<sub>2</sub> = 0.291 × 10<sup>-2</sup> M

The slopes of  $\log K_f \sim Z$  curves for MA-S copolymer are obviously larger than the slopes for MA-VAc copolymer. And also, at low value of  $Z$ , the  $\log K_f$  for MA-S copolymer are obviously smaller (this means the low stability of chelate ring) than the  $\log K_f$  for MA-VAc copolymer. The tendency is the same with Ba<sup>++</sup> and Ca<sup>++</sup>. At  $Z=1.3$ , which was relatively low value, the comparison of the formation constant  $\log K_f$  for MA-VAc copolymer with that for MA-S copolymer and also the results obtained by Morawetz were given in Table 3.

As is shown in Table 3, we can point out that the formation constant  $\log K_f$  for MA-VAc or for MA-VEE (maleic acid-vinyl ethyl ether) is larger than the  $\log K_f$  for MA-S at  $Z=1.3$ . However, at higher value of  $Z$ , the  $\log K_f$  for MA-VAc is smaller than the  $\log K_f$  for MA-S as is shown in Figs. 2 and 3.

Table 3 Comparison of chelate formation constants

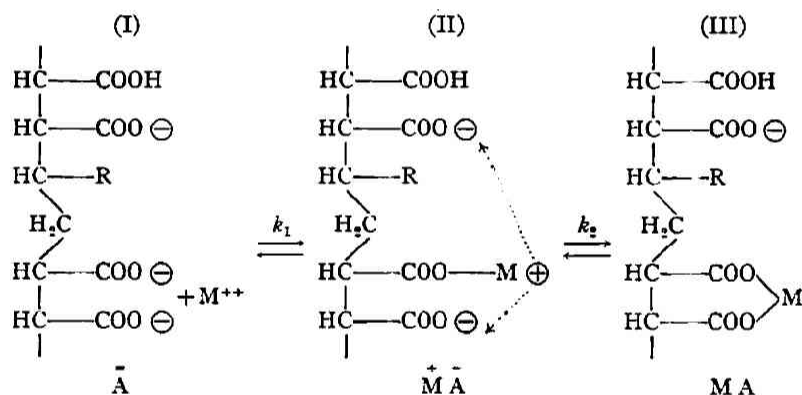
	Z	Ca <sup>++</sup>	Ba <sup>++</sup>	Temp., °C
MA-VAc	1.3	2.05	1.70	20
MA-S	1.3	1.78	1.36	20
MA-S*	1.3	2.11	1.36	25
MA-VEE*	1.3	2.45	2.00	25
succinic acid		1.16	0.76	25

\* Morawetz and co-workers; reference 3)

The titration was carried out in 1M KNO<sub>3</sub> solution with NaOH and the polymer concentration differed from that of the author.

These results may be interpreted by taking into consideration the influence of neighboring ionized groups beyond comonomer and the effect of all other ionized groups on a polymer chain.

The equilibrium defined by Reaction (2) is illustrated taking into consideration the influence of the neighboring ionized groups beyond comonomer;



In these figures, -R is -OCOCH<sub>3</sub> for MA-VAc copolymer, -C<sub>6</sub>H<sub>5</sub> for MA-S copolymer, and -OC<sub>2</sub>H<sub>5</sub> for MA-VEE copolymer. The intermediate state (II) corresponds to  $\text{M}^+ \text{A}^-$  in Reaction (2). These figures can be explained by dividing the formation constant  $K_f$  into two parts,  $k_1$  and  $k_2$ .

The positive ion, in the zwitterion  $\text{M}^+ \text{A}^-$  represented by (II), is subjected to the electrostatic attractive force of the neighboring negatively ionized carboxylate ion beyond the comonomer -CH<sub>2</sub>-CH(R)-, as well as of the negative ion within the zwitterion.

Thus, the smaller the screening effect of the comonomer is, the smaller the  $k_2$  value is. At the same time the effect makes the  $k_1$  value larger. However, as mentioned above, the contribution of entropy is obviously smaller for  $k_2$  than for  $k_1$ , so that the neighbor effect beyond the comonomer is larger on  $k_2$ . This is the reason why the formation constant for MA-S is smaller than that for MA-VAc or for MA-VEE at low Z value (Table 3).

As Z increases, the field effect of polyion increases, so that  $k_1$  becomes larger. The effect is obviously larger for MA-S than for MA-VAc, as is shown in Fig. 1. This is the reason why

the formation constant for MA-S is larger than that for MA-VAc at high  $Z$  value (Figs. 2 and 3).

All these effects are mainly due to the hydrophobic property of phenyl groups in the styrene copolymer.

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